

Electrical properties of polycrystalline materials from the system Cu-As-Ge-Se under high pressure condition

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Abstract. The paper deals with electrical properties of polycrystalline materials $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$ ($x = 0.5$ and 0.7) under high pressure (up to 45 GPa) conditions. The phenomenon of negative magnetoresistance was observed for studied materials.

1. Introduction

Multicomponent copper chalcogenides are actively studied materials due to their interesting from the fundamental and practical point of view electrical, optical and thermoelectrical properties [1-5]. The materials in the system Cu-As-Ge-Se demonstrate the electrical switching effects, which can be associated with the transition from an amorphous state to a crystalline state. In particular at small value of x , $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$ can be obtained in glassy and crystalline state, wherein glassy and crystalline materials with same composition have significant difference in electroresistance. Materials from the system $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$ are thermoelectric materials some of which have high value of thermoemf at high pressures up to 50 GPa [3].

This paper is devoted to study of high pressure influence (up to 45 GPa) on electrical properties of polycrystalline materials $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$, $x = 0.5$ and 0.7 , in constant electric field and in a transverse magnetic field (up to 1 T). The negative magnetoresistance phenomenon is investigated.

2. Materials and experiment details

Material $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$, $x = 0.7$, further Sample 1, crystallizes in cubic syngony, material $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$, $x = 0.5$, further Sample 2, crystallizes in tetragonal syngony [2]. More detail information about structure is presented in the table 1. The Sample 2 structure were detected by homology theory taking in account transformations of cubic lattice with Ge content changing in the system $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$.

Table 1. Crystal structure and the lattice parameters for Sample 1 and Sample 2.

	$(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$	Syngony	Lattice parameters
Sample 1	$x = 0.7$	Cubic	$a = 0.554 \text{ nm}$
Sample 2	$x = 0.5$	Tetragonal	$a = 0.394 \text{ nm}, c = 0.548 \text{ nm}$

High-pressure conditions were achieved with high-pressure cell with rounded cone-plane-type anvils made of carbonado-type artificial diamonds, which are good conductors with resistance less than



10 Ohm [6]. Detailed description of the pressure estimation method is presented in works [6, 7]. The powdered materials were used for high pressure measurements, the samples with a diameter of ~ 0.2 mm and thickness from 10 to 30 μm were obtained by the compression of powdered materials in the high-pressure cell. For magnetoresistance measurements the high-pressure cell was placed in the transverse magnetic field. The pressure and magnetic field were measured and controlled directly during the experiment. Magnetoresistance was calculated from the data obtained in experiment by formula (1)

$$MR = \frac{R_P(B) - R_P(0)}{R_P(0)} \quad (1),$$

where MR – magnetoresistance, $R_P(B)$ – electroresistance in fixed magnetic field and at fixed pressure, $R_P(0)$ – electroresistance at the corresponding pressure without magnetic field.

The Seebeck coefficient S was calculated by measuring the thermoelectromotive force (thermoemf) ΔU . For creation of temperature gradient ΔT one of the side of the sample was warmed. The accuracy of temperature measurements was about 0.05 K. Thermoemf measurements into interval 300–400 K at residual pressure of 0.1 Pa were carried out using ProboStat cell and the Solartron ModuLab Materials Test System, and the Seebeck coefficient was calculated by formula (2)

$$S = \frac{\Delta U}{\Delta T} \quad (2).$$

The Seebeck coefficient at high pressure conditions was calculated by measuring thermoelectromotive force induced in the sample via the copper branches of the thermocouples (used simultaneously for measurement the differences in the temperature between cold and hot faces of a sample) by formula (3)

$$S = S_{cu} + \frac{\Delta U}{\Delta T} \quad (3),$$

where S_{cu} – Seebeck coefficient of copper ($1.8 \mu\text{VK}^{-1}$).

3. Results and Discussion

Analysis of experimental results revealed significant (on 2 orders) electroresistance decreasing with pressure (P) increasing from 16 GPa to 42 GPa for both Sample 1 and Sample 2. The negative magnetoresistance (MR) phenomenon was observed for both materials and there are some extrema on curves $MR(P)$. Absolute value of negative MR increase with magnetic field increasing. Typical field dependences of MR at two fixed pressures (these pressures belong to the baric interval where $MR < 0$) for the Sample 1 are presented on figure 1.

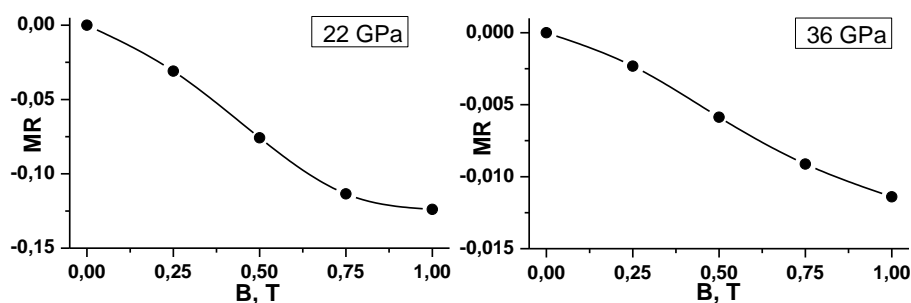


Figure 1. Field dependences of magnetoresistance for Sample 1 at pressures 22GPa and 36 GPa.

The electroresistance relaxation from applying the static pressure was studied for additional characterization of high pressure influence. It was found that electroresistance of studied materials decreases before achieving the constant (corresponding to applied pressure) level. The electroresistance relaxation curves can be approximated by exponential low in two ways. The first is approximation by standard decreasing exponential function (formula 4) and the second one, which is more accurate, is approximation by sum of two decreasing exponents (formula 5). When double exponential function is used for approximation, there are two relaxation times: smaller (t_1) and bigger (t_2), and using one exponent function for approximation, we get average relaxation time (t_a).

$$R = R_0 + a \cdot e^{-\frac{t_a}{t}} \quad (4)$$

$$R = R_0 + a \cdot e^{-\frac{t_1}{t}} + b \cdot e^{-\frac{t_2}{t}} \quad (5)$$

We can suggest that smaller relaxation time (t_1) corresponds to electroresistance relaxation process caused by carriers' concentration and band gap changes, and bigger relaxation time (t_2) corresponds to the relaxation process in lattice. The average relaxation time t_a at different pressures can be closer to either t_1 or t_2 . It means that at some pressures the relaxation of the electronic subsystem makes the main contribution to the whole relaxation process, at the other pressures – the relaxation of the lattice is prevailing. Curves $t_a(P)$ also have some extrema, herewith the baric intervals of $t_a(P)$ curves extrema correspond to the $MR(P)$ curves extrema (figure 2 and figure 3). Times of relaxation process corresponded to the changing of structure characteristics of crystal lattice (t_2) take their maximum values ($5 \cdot 10^3$ s for Sample 1 and $2 \cdot 10^3$ s for Sample 2) at pressure values corresponded to the $MR(P)$ extrema. Thus, we can assume that significant changes in crystal lattice cause changes in electronic structure, increase of carriers' concentration which in turn entails electroresistance decrease and manifests itself in appearance of $MR(P)$ extrema.

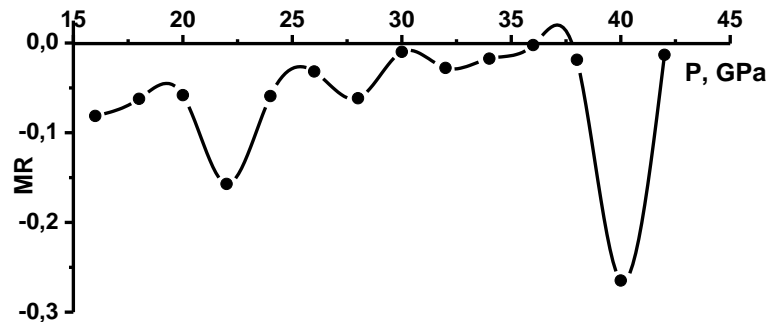


Figure 2. Baric dependence of magnetoresistance for Sample 2 at magnetic field 1 T.

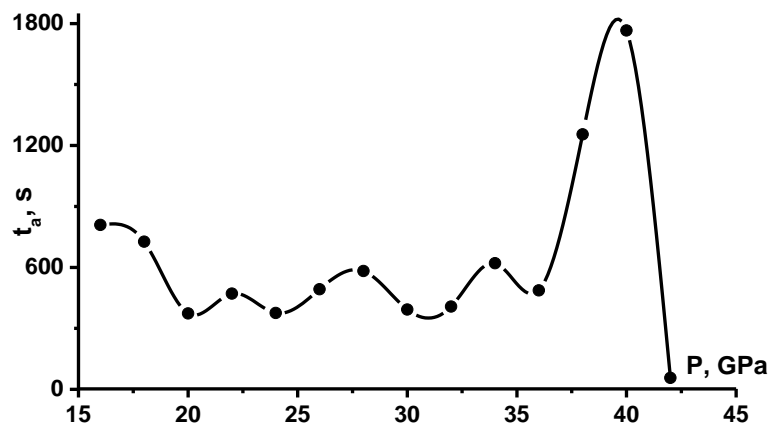


Figure 3. Baric dependence of average relaxation time (t_a) for Sample 2.

For studied materials, the extrema on curves $MR(P)$ correspond not only to the extrema on curve of relaxation time baric dependence, but also to the baric intervals of the other electrical properties significant changes. The MR baric dependence for Sample 1 has main extremum at pressure range 20-22 GPa (figure 4) and there are substantial changes in the electroresistance and in dielectric loss tangent behavior near 20-22 GPa (figure 5). The decreasing of electroresistance of Sample 1 almost ceases and the significant increase of dielectric loss tangent begin near 22 GPa.

Similar behavior of MR is known for materials CuInAsSe_3 and $(\text{GeS})_x(\text{CuAsS}_2)_{1-x}$, $x=0.7$ [8 – 10]. These materials can be obtained by replacement of germanium atoms with indium atoms in studied Sample 2 and by isovalent replacement of selenium atoms to sulfur atoms in Sample 1. As we can see in table 2, for both pair of materials the atoms replacing leads shift of $MR(P)$ extrema, wherein replacement of atoms by others with bigger radii shifts extrema on $MR(P)$ curve to the lower pressure ranges.

Table 2. Comparison of the pressure intervals in which the features MR behavior in the form of extrema were observed for studied materials CuGeAsSe_3 and $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$, $x=0.7$, and CuInAsSe_3 and $(\text{GeS})_x(\text{CuAsS}_2)_{1-x}$, $x=0.7$.

	CuAAsSe_3		$(\text{GeA})_x(\text{CuAsA}_2)_{1-x}$, $x=0.7$	
	A = In	A = Ge	A = S	A = Se
MR(P) extrema	20 GPa, 24 GPa, 36 GPa [8]	22 GPa, 26 GPa, 40 GPa	22-24 GPa [10]	20-22 GPa
A atomic radii	80 pm	73 pm	182 pm	193 pm

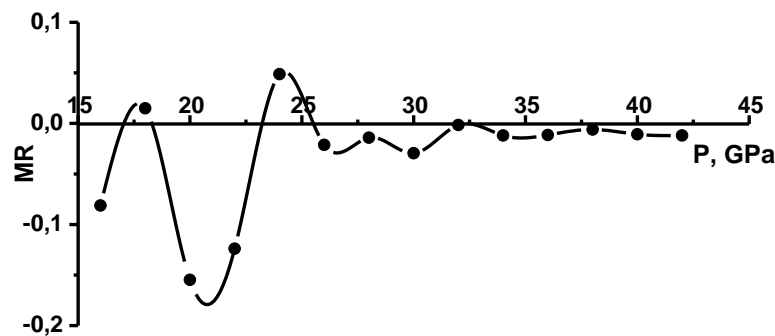


Figure 4. Baric dependence of the magnetoresistance for Sample 1 at magnetic field 1 T.

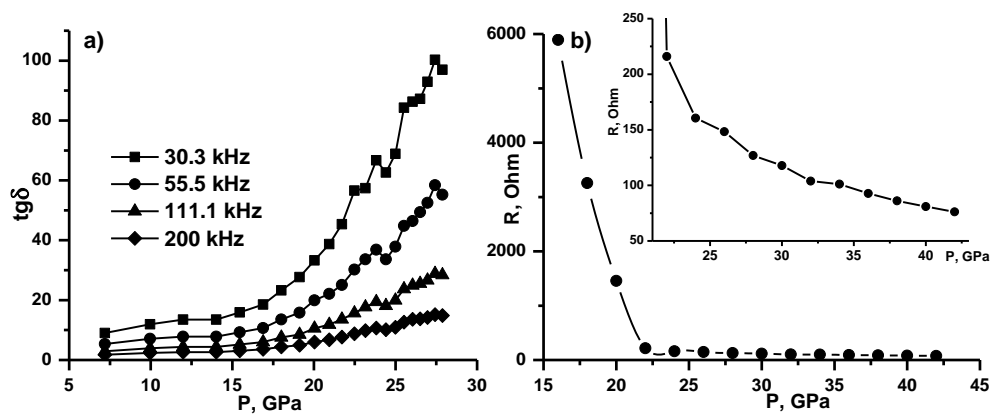


Figure 5. Baric dependences of a) dielectric loss tangent and b) the electroresistance for Sample 1.

Appearance of negative magnetoresistance for the material CuInAsSe_3 was explained by loose crystal structure, small number and mobility of carriers [8, 11]. The $MR(P)$ extrema for material $(\text{GeS})_x(\text{CuAsS}_2)_{1-x}$, $x=0.7$, can be related with significant lattice parameters changing (the results of X-ray studies under high pressure condition are presented in [10]). Because of the similarity of the crystal structures and the baric behavior of the studied properties (including pressure MR behavior) of the research materials to the corresponding parameters of CuInAsSe_3 and $(\text{GeS})_x(\text{CuAsS}_2)_{1-x}$, $x=0.7$, we can associate the negative magnetoresistance with the structure change and features of carriers behaviors

under high pressure. With pressure increasing the band gap can decrease, the carriers' concentration and mobility can change, as well as the effects determined by significant increase of numbers of defects and inhomogeneities, which are induced by deformation, can play significant role in *MR* behavior.

Exploration of carriers type and their behavior under pressure can help verify this assumption. By this reason, the study of thermoemf at atmospheric and high pressures and study of conductivity temperature dependence at some pressures were carried out for Sample 1.

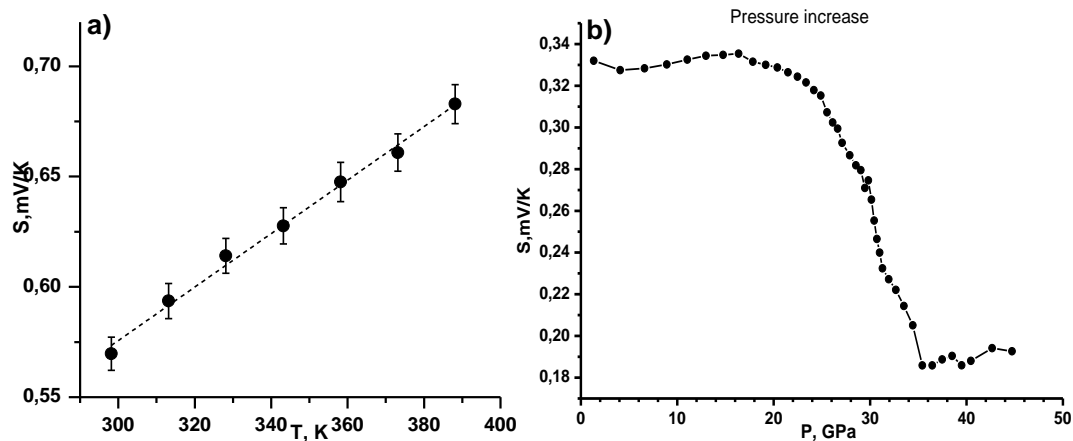


Figure 6. Dependences of Seebeck coefficient vs temperature at atmospheric pressure (a) and vs pressure at 298 K (b) for Sample 1.

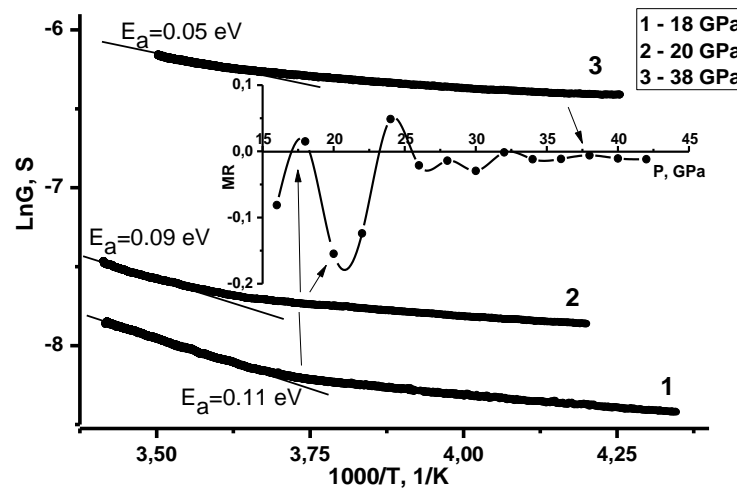


Figure 7. Temperature dependences of Sample 1 conductivity at pressures 18 GPa, 20 GPa and 38 GPa. On the insert the $MR(P)$ graph for Sample 1 is present.

The results of thermoemf study for Sample 1 at atmospheric pressure are presented at figure 6a. It is seen that studied material has high Seebeck coefficient value 0.57-0.68 mV/K into the temperature interval 298-388 K. Positive sign of thermoemf indicates that studied materials have p-type conductivity. Study of the temperature dependences of Sample 1 conductivity was carried out at pressures 18 GPa, 20 GPa and 38 GPa. These pressures correspond to the small positive value of MR , the main $MR(P)$ extremum, and the closeness of MR to zero (at $P > 32$ GPa) respectively (figure 7). At all investigated pressures, material is characterized by activation type of conductivity, the activation energy values at room temperature are presented in figure 7. It is seen that the activation energy decreases with increasing

pressure, we can assume that band gap becomes narrower and at pressures bigger 32 GPa MR weakly depends on pressure.

The results of pressure dependence of thermoemf for Sample 1 are presented on figure 6b. Material has high value of thermoemf at high pressure. The thermoemf decreases with pressure increasing but saves its sign. We can see correlation between significant changes in MR (figure 4) and thermoemf behaviors. Baric interval 20-22 GPa corresponds to the main extremum on $MR(P)$ curve and beginning of thermoemf decreasing. After 32-34 GPa MR becomes close to zero and thermoemf achieves its minimum and almost stops changing as well as MR .

Described results of thermoemf studies and conductivity temperature studies let us make the following conclusions and confirm assumption made above. With increasing of pressure and deformation of the crystal lattice the defect number increases, the activation energy decreases, the band gap decreases, which manifest themselves in high negative magnetoresistance. Summarizing all described above, the phenomenon of negative magnetoresistance and presence of $MR(P)$ extrema with high negative value of MR in the studied materials are caused by significant changes in the crystal and the electronic structures with pressure increasing.

4. Conclusions

The experimental study of electrical properties of $(\text{GeSe})_x(\text{CuAsSe}_2)_{1-x}$, $x = 0.5$ and 0.7 , at high pressure shows that electroresistance of studied materials decreases with the pressure increasing and both materials exhibit the negative magnetoresistance in studied pressure range. Magnetoresistance pressure dependences have some extrema which correspond to the baric intervals of features in the other electrical properties behaviors (electroresistance, dielectric loss tangent, electroresistance relaxation time, thermoemf). The suggestion that phenomenon of negative magnetoresistance and magnetoresistance extrema presence in studied materials are due to significant changes in the crystal and the electronic structures with pressure was made.

Acknowledgments

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